

Ideal Gas in a Finite Container*

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A common practice in many statistical thermodynamics textbooks when calculating the partition function, is to replace the relevant statistical sums by integrals over a quasicontinuum of levels, right at the outset.¹ Since the interlevel separation is inversely proportional to the system's size, when doing that, they are really assuming an infinite system, and washing away any finite size effects. This, of course, simplifies the problem at hand, but at the same time obscures the manner in which size effects enter when dealing with finite systems. In this Note, we illustrate the role of finite size effects by evaluating the main corrections to the canonical partition function of the ideal gas due to a large, yet finite, container volume.

Sufficient conditions under which it is valid to replace sums by integrals have been examined by Stutz² using the Euler summation formula. For the case of the one-particle, one-dimensional partition function, Fox³ rederived Stutz results by using the Jacobi transformation. In the spirit of Fox, we will express the partition function of a three-dimensional ideal gas enclosed in a impenetrable box in terms of complete elliptic integrals of the first kind, whose argument obeys a transcendental equation, and will explicitly derive the main finite volume corrections to thermodynamical quantities. A different approach will be followed for the case of an impenetrable spherical container, where we will expand the density of states in powers of the energy. Surface terms appear in the expansion coefficients, leading to finite size effects in the thermodynamics of the system.

We will find that, for both, the box and the spherical container, the finite volume correction terms to thermodynamical quantities, have the *same* functional dependence on the ratio (thermal wavelength \times area/volume).

Ideal gas in a box: Consider an ideal monoatomic gas of N identical particles of mass m , enclosed in a box with sides a_1 , a_2 and a_3 , at temperature T . We will assume a gas temperature (density) high (low) enough so that the Boltzmann statistics is applicable. In those conditions, the partition function is given by⁴

$$Z = [z]^N / N! \quad (1)$$

with

$$z = \prod_{i=1}^3 \sum_{n_i=1}^{\infty} \exp(-\sigma_i n_i^2) \quad (2)$$

and

$$\sigma_i = \frac{3}{8} \left(\frac{\lambda(T)}{a_i} \right)^2 \quad (3)$$

where $\lambda(T) = h/\sqrt{3mk_B T}$ is the de Broglie thermal wavelength and k_B , h are the Boltzmann and Planck constants, respectively. At room temperature, the spacing between two consecutive arguments in the exponential is very small (of the order of 10^{-10} for $m = 10^{-22}$ g, $a_i = 10$ cm and $T = 300$ K). However, since σ_i depends on the inverse of the product *temperature \times (linear size of the system)²*, according to Eq.(3), there are situations, such as small volumes (“molecular cavities”) where such spacing, while still small, can grow considerably (of the order of 10^{-3} for $T = 1$ K and $a_i = 10^{-5}$ cm).

The function we are interested in is the infinite sum

$$s(\sigma) = \sum_{n=1}^{\infty} \exp(-\sigma n^2) \quad (4)$$

which is a special case of the more general type of sum $\sum_{n=1}^{\infty} q^{n^2}$ with $|q| < 1$.

This sum can be expressed in terms of the *theta function*⁵

$$\theta_3(0, q) = 1 + 2q + 2q^4 + 2q^9 + \dots \quad (5)$$

From the identity⁶ $(2K/\pi)^{1/2} = \theta_3(0, q)$, we have

$$s(\sigma) = \frac{1}{2} \left[\left(\frac{2K(k)}{\pi} \right)^{1/2} - 1 \right] \quad (6)$$

where $K(k)$ is the complete elliptic integral of the first kind

$K(k) = \int_0^{\pi/2} d\alpha (1 - k \sin(\alpha)^2)^{-1/2}$ and the argument k satisfies the transcendental equation⁷

$$K(1 - k) - (\sigma/\pi)K(k) = 0 \quad (7)$$

Fig.1 shows the plot of $K(1 - k)$ and $(\sigma/\pi)K(k)$ for different values of (σ/π) .

As soon as (σ/π) deviates slightly from unity, the intersection of the two curves tends to occur very close to either $k = 0$ or $k = 1$, which justifies a perturbation expansion around those points.

At high temperatures (or large container dimensions) $(\sigma/\pi) \ll 1$ and the root of eq.(7) lies close to $k = 1$, which implies, according to eq.(7), $K(k) \approx (\pi/\sigma)K(0) = \pi^2/2\sigma$. After inserting this into eq.(6), we obtain

$$s(\sigma) \approx \frac{1}{2} \left[\left(\frac{\pi}{\sigma} \right)^{1/2} - 1 \right] \quad (8)$$

This approximation differs slightly from the standard textbook⁸ expression $s(\sigma) = (1/2)(\pi/\sigma)^{1/2}$. Table I shows a comparison of both expressions with the exact result. We see that eq.(8) shows better agreement up to values of σ as high as $\sigma \sim 1$. After inserting Eq.(8) into Eqs.(2) and (1), we have,

$$\begin{aligned}\log(Z) &\approx N \log \left[\frac{1}{8} \left(\frac{\pi^3}{\sigma_1 \sigma_2 \sigma_3} \right)^{1/2} \frac{e}{N} \right] + N \sum_{i=1}^3 \log \left(1 - \left(\frac{\sigma_i}{\pi} \right)^{1/2} \right) \\ &\approx N \log \left[\frac{1}{8} \left(\frac{\pi^3}{\sigma_1 \sigma_2 \sigma_3} \right)^{1/2} \frac{e}{N} \right] - N \sum_{i=1}^3 \left(\frac{\sigma_i}{\pi} \right)^{1/2}\end{aligned}\quad (9)$$

We are now in position to evaluate the main corrections to the energy $U = k_B T^2 (\partial \log(Z) / \partial T)_{N,V}$, pressure $P = k_B T (\partial \log(Z) / \partial V)_{N,T}$, specific heat $C = (\partial U / \partial T)_{N,V}$ and entropy $S = k_B \log(Z) + k_B T (\partial \log(Z) / \partial T)_{N,V}$. We obtain :

$$\text{Energy:} \quad U \approx U_0 \left[1 + \frac{1}{\sqrt{96\pi}} \left(\frac{\lambda(T)A}{V} \right) \right] \quad (10)$$

where $U_0 = (3/2)Nk_B T$ and $A = 2(a_1 a_2 + a_1 a_3 + a_2 a_3)$ is the area of the box and $V = a_1 a_2 a_3$ is its volume.

$$\text{Pressure :} \quad P \approx P_0 \left[1 + \frac{1}{\sqrt{96\pi}} \left(\frac{\lambda(T)A}{V} \right) \right] \quad (11)$$

where $P_0 = Nk_B T / V$.

$$\text{Specific Heat:} \quad C \approx C_0 \left[1 + \frac{1}{\sqrt{384\pi}} \left(\frac{\lambda(T)A}{V} \right) \right] \quad (12)$$

where $C_0 = (3/2)Nk_B$.

$$\text{Entropy:} \quad S \approx S_0 - \sqrt{\frac{3}{128\pi}} Nk_B \left(\frac{\lambda(T)A}{V} \right) \quad (13)$$

where

$$S_0 = (3/2)Nk_B + Nk_B \log \left[\frac{1}{8} \left(\frac{\pi^3}{\sigma_1 \sigma_2 \sigma_3} \right)^{1/2} \frac{e}{N} \right]. \quad (14)$$

Thus, the main correction due to the finite volume of the container has the form (thermal wavelength \times area/volume).

Ideal gas in spherical container: Let us now consider the same ideal gas of the preceding section enclosed in a spherical container of radius R . The eigenvalue equation is : ⁹ $j_l(kR) = 0$ with $l = 0, 1, 2, \dots$ where $k = (8\pi^2 m E / h^2)^{1/2}$ and $j_l(x)$ is a spherical Bessel function. For each l , we have an infinite number of solutions, indexed by an integer $n = 1, 2, \dots$ and for each (l, n) we have an angular momentum degeneracy of $(2l + 1)$. The energies are $E_{ln} = (h^2 / 8\pi^2 m R^2) X_{ln}^2$, where X_{ln} is the n th root of $j_l(x)$. In the limit of large R , we can approximate the X_{ln} using McMahon's expansion: ¹⁰

$$X_{ln} = b - \frac{(\mu - 1)}{8b} - \frac{4(\mu - 1)(7\mu - 31)}{3(8b)^3} - \frac{32(\mu - 1)(83\mu^2 - 982\mu + 3779)}{15(8b)^5} - \frac{64(\mu - 1)(6949\mu^3 - 153855\mu^2 + 1585743\mu - 6277237)}{105(8b)^7} + \dots \quad (15)$$

with $\mu \equiv (2l + 1)^2$ and $b \equiv (n + (l/2))\pi$.

Now, instead of using Eq.(15) to calculate directly the atomic partition function, we will use it to evaluate the *density of states*, which is all we need to calculate the thermodynamic properties of the system. For a container of “simple” shape it is natural to expect that the main contributions to the density of states will have the form:

$$\rho(E) \approx \rho_1 E^{1/2} + \rho_2 + \rho_3 E^{-1/2} \quad (16)$$

where each term has the typical form of a three, two, and one dimensional density of states. The relative importance of each term in Eq.(16) will depend upon the “dimensionality” of the container. Thus, for our spherical container where “volume” predominates over “area” and “length”, the main contribution comes from the term proportional to $E^{1/2}$, with a small (constant) correction term. In this case, it is convenient to rewrite Eq.(16) in terms of dimensionless parameters R_1, R_2 :

$$\rho(E) \approx (3/2)R_1 \left(\frac{h^2}{8\pi^2 m R^2} \right)^{-3/2} E^{1/2} + R_2 \left(\frac{h^2}{8\pi^2 m R^2} \right)^{-1} \quad (17)$$

where we have kept only the surface correction term. We proceed as follows: Starting from Eq.(15), we evaluate numerically the integrated density of states $\phi(E)$, defined as the number of states with energies less than E . Then, we perform a least-squares fit of the resulting histogram to the smooth function

$$\phi(E) = R_1 \left(\frac{h^2}{8\pi^2 m R^2} \right)^{-3/2} E^{3/2} + R_2 \left(\frac{h^2}{8\pi^2 m R^2} \right)^{-1} E \quad (18)$$

obtaining the optimal values for R_1, R_2 . The approximate density of states is then given by Eq.(17).

The atomic partition function is given by

$$z = \int_0^\infty dE \quad \rho(E) e^{-\beta E}. \quad (19)$$

By using Eqs.(17),(19) and the numerical values obtained for R_1, R_2 , we can write the main corrections to several thermodynamics quantities:

$$\text{Energy:} \quad U \approx U_0 \left[1 + 0.0461 \left(\frac{\lambda(T)A}{V} \right) \right] \quad (20)$$

where $U_0 = (3/2)Nk_B T$ and A, V are the area and volume of the sphere, respectively.

$$\text{Pressure :} \quad P \approx P_0 \left[1 + 0.0461 \left(\frac{\lambda(T)A}{V} \right) \right] \quad (21)$$

where $P_0 = Nk_B T/V$.

$$\text{Specific Heat:} \quad C \approx C_0 \left[1 + 0.02305 \left(\frac{\lambda(T)A}{V} \right) \right] \quad (22)$$

where $C_0 = (3/2)Nk_B$.

$$\text{Entropy:} \quad S \approx S_0 - 0.0693Nk_B \left(\frac{\lambda(T)A}{V} \right) \quad (23)$$

where

$$S_0 = (3/2)Nk_B + Nk_B \log \left[2.804 \left(\frac{8mR^2k_B T}{h^2} \right)^{3/2} \frac{e}{N} \right]. \quad (24)$$

The method outlined above for the sphere can be used for any other container of “simple” shape, provided the eigenenergies are known either analytically or numerically. To its conceptual simplicity we have to oppose its rather slow numerical convergence, requiring very many energies to obtain coefficients with a given accuracy.

As in the case of the box, the main finite volume corrections for the sphere have the form *constant* \times (thermal wavelength \times area/volume). For

both, the box and the spherical container, the thermodynamical quantities U_0, P_0, C_0 and S_0 do not depend on the shape of the container. The main finite size corrections have the *same* functional dependence on the ratio (thermal wavelength \times area/volume) for both shapes.

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¹ See, for instance, Donald A. McQuarrie, *Statistical Mechanics*, (Harper and Row, New York, 1976), p. 82.

² C. Stutz, “On the Validity of Converting Sums to Integrals in Quantum Statistical Mechanics”, Am. J. Phys. **36**, 826-829 (1968).

³ K. Fox, “Comment on: ‘On the Validity of Converting Sums to Integrals in Quantum Statistical Mechanics’ ”, Am. J. Phys. **39**, 116-117 (1971).

⁴ Reference 1, p. 81.

⁵ M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*, (Dover, New York, 1965), p.576.

⁶ Reference 5, p. 579.

⁷ Reference 5, p. 591.

⁸ Reference 1, p. 82

⁹ L.D. Landau and E.M. Lifshitz, *Quantum Mechanics* (Pergamon, Oxford, New York, 1977), 3rd ed., p. 111.

¹⁰ Reference 5, p. 371.

Captions List

Fig.1 : Complete elliptic integral of the first kind. The continuous line is $K(1-k)$, while the dashed, dotted and dot-dashed curves are $(\sigma/\pi)K(k)$ for $(\sigma/\pi) = 0.5, 1$ and 2 , respectively.

Table I Particle in a box: Comparison of the exact atomic partition function $s(\sigma)$ (second column) with approximation (8) (third column) and with the standard approximation for high temperatures (fourth column).

σ	$\sum_{n=1}^{\infty} e^{-\sigma n^2}$	$\frac{1}{2} \left[\left(\frac{\pi}{\sigma} \right)^{1/2} - 1 \right]$	$\frac{1}{2} \left(\frac{\pi}{\sigma} \right)^{1/2}$
1	0.38631860	0.38622693	0.88622693
0.5	0.75331414	0.75331413	1.25331414
0.1	2.30249561	2.30249561	2.80024956
0.01	8.36226926	8.36226926	8.86226926
0.001	27.5249561	27.5249561	28.0249561
0.0001	88.1226926	88.1226926	88.6226926
0.00001	279.749561	279.749561	280.249561

